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Title: PLASTIC CONTAINER HAVING A CARBON-TREATED INTERNAL SURFACE

TECHNICAL FIELD

The present invention relates to plastic containers based on recycled plastic. More particularly, the present invention relates to blow molded plastic containers based on recycled plastic, having barrier properties and having a carbon-coated internal surface.

BACKGROUND ART

It is highly desirable to provide plastic containers having barrier properties, and it is also highly desirable to provide plastic containers using recycled plastic. However, recycled plastic generally does not have barrier properties and cannot be used in containers in direct contact with container contents. Therefore, despite the economic desirability of using recycled plastic, the use of such material has been difficult.

Conventionally, the use of recycled plastic in containers especially those holding contents for human consumption has been limited to multi-layer plastic containers where the recycled plastic is an outer layer which does not come into direct contact with the container contents.

Multi-layer plastic containers are commonly used for packaging items in a wide range of fields, including food and beverage, medicine, health and beauty, and home products. Plastic containers are known for being easily molded, cost competitive, lightweight, and generally suitable for many applications. Multi-layered containers provide the benefit of being able to use different materials in each of the layers, wherein each material has a specific property adapted to perform a desired function.

Because plastic containers may permit low molecular gases, such as oxygen and carbon dioxide, to slowly permeate through their physical configurations, the use of plastic containers

sometimes proves to be less desirable when compared to containers formed from other less permeable materials, such as metal or glass. In most applications, the shelf life of the product contents is directly related to the package's ability to effectively address such molecular permeation. In the case of carbonated beverages, such as beer, oxygen in the atmosphere surrounding the container can gradually permeate inwardly through the plastic walls of the container to reach the inside of the container and deteriorate the contents. Likewise, carbon dioxide gas associated with the contents may permeate outwardly through the plastic walls of the container until eventually being released on the outside, causing the carbonated beverage to lose some of its flavor and possibly become "flat".

To address some to the foregoing concerns, plastic container manufacturers have utilized various techniques to reduce or eliminate the absorption and/or permeability of such gases. Some of the more common techniques include: increasing the thickness of all or portions of the walls of the container; incorporating one or more barrier layers into the wall structure; including oxygen-scavenging or reacting materials within the walls of the container; and applying various coatings to the internal and/or external surface of the container. However, a number of conventional barrier and/or scavenger materials will not effectively curtail the permeation of both oxygen and carbon dioxide over extended periods of time. Moreover, there are usually other practical concerns associated with most conventional techniques, most commonly, increased material costs and/or production inefficiencies.

In recent times, the use of plastics has become a significant social issue. Recycling has become an increasingly important environmental concern and a number of governments and regulatory authorities continue to address the matter. In a number of jurisdictions, legislation pertaining to minimum recycled plastic content and the collection, return, and reuse of plastic containers has either been considered or has already

been enacted. For example, in the case of plastic containers used to hold consumable items, such as food items or beverages, regulations often require a certain content and minimum thickness of the innermost layer that comes in contact with the contents. Conventional processes, such as co- or multiple-injection molding, are often limited as to the amount of recycled plastic that can be effectively incorporated into the structure of the container. Commonly, the amount of recycled content that can be effectively incorporated into conventional co-injection molded containers that are suitable for food contents is less than 40% of the total weight of the container.

Therefore, a need exists in the industry and it is an object of the present invention to provide a plastic container having a high recycled content that is suitable for holding carbonated products, such as carbonated beverages, and provide an acceptable level of performance when compared to commercial containers formed from alternative materials. A further need exists for a method to produce such containers in high volume commercial rates using conventional equipment.

It is a still further object of the present invention and need to provide a container based on recycled plastic which has barrier properties and which minimizes or avoids the high cost of inconvenience of conventional multi-layer plastic containers. It is a still further objective to do this at a reasonable cost, in a commercially feasible process, and with an effective product.

SUMMARY OF INVENTION

It has been found that the foregoing objects and advantages are readily obtained in accordance with the present invention.

Recognizing the problems and concerns associated with conventional multi-layered plastic containers, especially those used to hold carbonated beverages, a plastic container having enhanced gas barrier properties and a high content of recycled plastic is advantageously provided. A container constructed in

accordance with the principles of the present invention provides several advantages over those previously available. Such advantages are generally realized through the use of the desirable recycled plastic and a carbon coating on the internal surface of the container. It is a significant advantage that the container of the present invention desirably may have a significant amount of recycled content. Furthermore, the improved container can be produced using conventional processing techniques and manufacturing equipment.

An important aspect of the present invention is the effective barrier properties of the present container with the functional and commercial benefits associated with having a container comprised a significant amount of recycled plastic content. Further, the ease in subsequently recycling a container produced in accordance with the principles of the present invention make the practice of the invention extremely advantageous. Moreover, the present invention provides the additional advantage of permitting the manufacturer to controllably vary the material positioning and wall thickness at any given location along the vertical length of the inner and/or outer layers of the container.

In accordance with the principles of the present invention, a blow molded multi-layer container is provided having an upper wall portion, an intermediate sidewall portion positioned beneath the upper wall portion, and a base portion positioned beneath the intermediate sidewall portion, the base portion being adapted to dependently or independently support the container. The container includes a molded outer layer formed from recycled plastic and a carbon coating adjacent and desirably on the inner surface of the molded outer layer that is substantially coextensive with the inner layer. The recycled outer layer comprises at least 40% by weight of recycled plastic, but can comprise more than 75% by weight and desirably more than 90% by weight, depending upon the needs of the application. In a preferred embodiment, the thickness of the

outer layer is controllably adjusted along its vertical length. If desirable, the outer layer may also include additional barrier materials and/or oxygen scavenging/reacting materials incorporated therein.

In accordance with the principles of the present invention, a blow molded multilayer container is also provided having an upper wall portion, an intermediate sidewall portion positioned beneath the upper wall portion, and a base portion positioned beneath the intermediate sidewall portion, the base portion being adapted to dependently or independently support the container. The container includes (i) a molded inner layer formed from a plastic material, the inner layer having a vertical length and a carbon-treated inner surface; and (ii) a molded outer layer formed from recycled plastic that is substantially coextensive with the inner layer. The recycled outer layer comprises at least 40% by weight of the overall weight of the container, but can comprise more than 90% by weight, depending upon the needs of the application. In a preferred embodiment, the thickness of the inner and/or outer layers is controllably adjusted along their respective vertical lengths. If functionally desirable, the inner layer and/or outer layer may also include additional barrier materials and/or oxygen scavenging/reacting materials.

Other and further advantages and novel features of the invention are readily apparent from the following detailed description of the best mode for carrying out the invention when taken in connection with the accompanying drawings, wherein, by way of illustration and example, embodiments of the present invention are disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be more readily understandable from consideration of the accompanying drawings, wherein:

FIG. 1 is an elevation view of a container in accordance with the principles of the present invention.

FIGS. 1A, 1B and 1C are cross-sectional and enlarged views of various areas of the container wherein the relative thicknesses of the layers forming the container are illustrated.

FIG. 2 is a partially broken away elevation view of one examples of a multi-layer preform.

FIG. 3 is a partially broken away elevation view of another example of a multi-layer preform.

FIG. 4 is an elevation view of a container in accordance with the principles of the present invention.

FIGS. 5, 6 and 7 are cross-sectional and enlarged views of various areas of the container wherein the relative thicknesses of the layers forming the container are illustrated.

FIG. 8 is a partially broken away elevation view of one example of a preform.

FIG. 9 is a partially broken away elevation view of another example of a preform.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Referring now to the drawings in detail, wherein like reference numerals and letters designate like elements, there is shown in FIG. 1 an elevational view of a container 10 constructed in accordance with the principles of the present invention. Container 10 typically includes an upper wall portion 12, including an opening 13; an intermediate sidewall portion 14 positioned beneath the upper wall portion 12; and a base portion 16 positioned beneath the intermediate sidewall portion 14. The base portion 16 is adapted to support the container 10 either dependently, i.e., where another object such as a base cup (not shown) is used, or independently, i.e., where no other objects are needed to stand the container upright on a generally flat surface. In a preferred embodiment, the container 10 is supported by a freestanding base formed by a plurality of integrally formed feet 18, such as those illustrated in FIG. 1.

Referring to FIGS. 1A-1C, which represent enlarged detailed views of areas 1A, 1B and 1C, respectively, of FIG. 1, the container 10 includes (a) a molded inner layer 20, having a vertical length and an inner surface 22; (b) a molded outer layer 24; and (c) a central vertical axis A. The inner surface 22 of the molded inner layer 20 is at least partially coated with a thin layer or film of carbon 26. While complete encapsulation of the inner layer 20 by the outer layer 24 is not required, it is preferred that the molded outer layer 26 is substantially coextensive with the inner layer 20 and provides structural support to the walls of the container 10.

The molded inner layer 20 is comprised of a thermoplastic material. The following resins may be used as plastic materials for the inner layer 20: polyethylene resin, polypropylene resin, polystyrene resin, cycloolefine copolymer resin, polyethylene terephthalate resin, polyethylene naphthalate resin, ethylene-(vinyl alcohol) copolymer resin, poly-4-methylpentene-1 resin, poly (methyl methacrylate) resin, acrylonitrile resin, polyvinyl chloride resin, polyvinylidene chloride resin, styrene-acrylo nitrile resin, acrylonitrile-butadiene-styrene resin, polyamide resin, polyamideimide resin, polyacetal resin, polycarbonate resin, polybutylene terephthalate resin, ionomer resin, polysulfone resin, polytetra fluoroethylene resin and the like. When food product contents are involved, the inner layer 20 is preferably formed from virgin polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and/or blends of polyethylene terephthalate and polyethylene naphthalate. However, other thermoplastic resins, particularly those approved for contact with food products, may also be used.

The molded outer layer 24 is comprised of a recycled plastic material, including the plastics set forth in the preceding paragraph, but is commonly formed from recycled polyethylene terephthalate (PET). However, the invention is not

limited to a particular type of recycled plastic and other recycled plastic materials may be used.

In a preferred embodiment, the inner layer 20 has a wall thickness, taken along its vertical length, that is in the range of 0.5 mil to 5 mil (0.0127 mm to 0.127 mm) and more preferably between 1 to 2 mils (0.0254 mm to 0.0508 mm). In some instances, such as where food product contents are involved, a minimum thickness requirement for the inner layer 20 may be specified and must be met. As illustrated in FIG. 1 and FIGS. 1A, 1B and 1C, the thickness of the inner layer may be varied along the vertical length. In this manner, different portions of the container 10 can have variably controlled thickness along the vertical length, providing improved material usage and increased design flexibility. For instance, the thickness of the inner layer 20 positioned at the upper portion 12 (such as shown in FIG. 1A) can be thinner than the intermediate sidewall portion 14 (such as shown in FIG. 1B). Likewise, the thickness of the inner layer 20 at the base wall portion 16 (such as shown in FIG. 1C) can be thicker than the thickness of the same layer in the intermediate sidewall portion 14 (such as shown in FIG. 1B).

In keeping with an aspect of the present invention, the inner layer comprises less than 0.60 by weight of the total weight of the container 10, preferably less than 0.30 of the total weight of the container 10, and more preferably, less than about 0.15 of the total weight of the container 10. The ability of the present invention to utilize an exceptionally thin inner layer 20 -- particularly when compared to other conventional multi-layer containers -- can provide significant economic advantages and incentives, especially in instances in which virgin material is more costly and/or scarce than recycled material.

As mentioned earlier, the inner surface 22 of the inner layer 20 is coated with a thin layer of carbon 26 which provides enhanced barrier properties to the container 10. In a preferred

embodiment, the carbon coating 26 is comprised of a highly hydrogenated amorphous carbon that is doped with nitrogen. The thickness of the carbon coating 26 is less than about 10 μm and the weight of the coating 26 is less than about 1/10,000th of the total weight of the container. An important feature of the present invention is than only about 3 mg of the carbon coating 26 is needed to treat a 500 cc plastic container. Further, despite the notable thinness of the carbon coating 26, the amount of barrier protection afforded is quite significant and the protection from permeation of oxygen and carbon dioxide is favorable when compared with the protection found in metal cans and glass bottles. Initial tests have shown that the barrier provided in connection with the present invention against oxygen permeation can be more than thirty times better than that of a container formed from untreated PET; the barrier provided against carbon dioxide permeation can be more than seven times better than that of a container formed from untreated PET; and the barrier provided against the migration of total aldehydes can be more than six times better than untreated PET.

The molded outer layer 24 comprises at least about 0.40 by weight of the total weight of the container 10, but can comprise more than 0.90 by weight of the total weight of the container 10 for certain applications. In a preferred embodiment, the outer layer 24 has a wall thickness, taken along its vertical length, that is in the range of 6 to 23 mils (0.1524 mm to 0.5842 mm). As illustrated in FIG. 1 and FIGS. 1A, 1B and 1C, the thickness of the outer layer can also be separately and independently varied along its vertical length. In this manner, different portions of the container 10 (taken perpendicular to the central vertical axis A) can have different inner layer thicknesses, different outer layer thicknesses, and/or different overall thickness measurements, all by design. For instance, the thickness of the molded outer layer 24 positioned at the upper portion 12 (such as shown in FIG 1A) can be much thicker than the intermediate sidewall portion 14 (such as shown in FIG. 1B).

Likewise, the thickness of the outer layer 24 at the base wall portion 16 (such as shown in FIG. 1C) can be thicker than the thickness of the same layer in the intermediate sidewall portion 14 (such as shown in FIG. 1B). Because the molded outer layer 24 is generally comprised of a less expensive plastic material that does not directly contact the contents of the container 10, a less expensive material can be used to form a number of the structural integral components for the container, such as the neck flange 30 and outer threads 30 shown in FIG. 1 and FIG. 1A.

While it is often unnecessary -- and can complicate the recycling process -- in special applications, the inner layer 20 and/or outer layer 24 may further include additional barrier materials and/or oxygen scavenging/reacting materials (not shown) that are commonly known in the art. Examples of some of the more commonly used barrier materials include saran, ethylene vinyl alcohol copolymers (EVOH), and acrylonitrile copolymers, such as Barex. The term saran is used in its normal commercial sense to contemplate polymers made for example by polymerizing vinylidene chloride and vinyl chloride or methyl acrylate. Additional monomers may be included as is well known. Vinylidene chloride polymers are often the most commonly used, but other oxygen barrier materials are well known. Oxygen-scavenging materials can include materials marketed for such a purpose by several large oil companies and resin manufacturers. A specific example of such a material is marketed under the trade name AMOSORB and is commercially available from the Amoco Corporation.

Another significant advantage of the present invention is its ability to provide significant barrier properties, incorporate a high content of recycled plastic material, and be advantageous to present day recycling. The inner layer 20 and outer layer 24 are both comprised of plastic material and can be readily recycled. Unlike a number of other barrier materials often used in connection with multi-layer containers, which can be difficult to separate, the carbon coating 26 of the present

invention has no impact on the recycling of the plastic materials of which the container 10 is comprised.

The present invention includes the additional advantage of being able to provide a container 10 with enhanced barrier properties that can be used for holding food products. Plastic containers having an inner surface treated with an amorphous carbon film have been approved for contact with food products from the Technische National Onderzoek, the standards organization accredited by the European Economic Community. The approval of the United States Food and Drug Administration (USFDA) is currently in process.

The container 10 of the present invention may be formed by any of several known processing techniques which permit the manufacture of a multi-layer blow molded container 10 having a plastic molded inner layer 20 and a relatively thick molded outer layer 24 of recycled plastic. In a preferred embodiment, the multi-layer container 10 is formed via a blow molding operation involving a multi-layer preform 34, such as the one generally depicted in FIG. 2. Although not a required feature, the preform 34 may include a neck flange 30 (for handling purposes) and outer threads 32 (to secure a closure) that correspond to the same features shown in FIG. 1. After the blow molding of the container 10, as shown in FIG. 1, but some time before the filling operation, the inner surface 22 of the inner layer 20 of the container 10 is carbon-treated as further discussed below.

In a first preferred embodiment, as shown in FIG. 2, the preform 34 is produced by extrusion molding an inner layer 20' having an inner surface 22' thereof and injection molding an outer layer 24'. The inner layer 20' and outer layer 24' of the preform 34 correspond to the inner layer 20 and outer layer 24 of the container 10. Extrusion of the inner layer 20' of the preform allows the manufacturer to produce a thinner layer than is generally possible using conventional injection molding or co-injection processes. For example, the inner layer of an

extrusion molded multi-layer preform 34 may be made as thin as 15-20 mils (.381 mm to 0.508 mm) or less. Conversely, it is difficult, if not impossible, to reliably injection mold an inner layer having a comparable thickness profile. Further, an extrusion or co-extrusion process permits the manufacturer to readily vary the thickness of material being extruded along the length of the extrudate. Variations in the thickness of the inner layer is desirable for several reasons which include aesthetics, efficient material use and reduced costs, and variable strength requirements.

The outer layer 24' of the preform 34 is formed from a recycled plastic material and, in accordance with the present invention, is substantially thicker than the inner layer 20'. The outer layer 24' can be injection molded or compression molded over the inner layer 20', although injection molding is generally preferred. Such over-molding processes further permit the formation of a neck flange 30 and outer threads 32.

In a second preferred embodiment, the multi-layer preform 34 is produced by thermoforming a thin sheet of plastic material and forming that sheet into what will become the inner layer 20' having an inner surface 22' thereof of the preform 34. The process of thermoforming permits the formation of a preform 34 with a very thin inner layer 20'. In fact, minimum wall thicknesses of 3 mil (0.0762 mm) or less are possible. As in the case of an extruded inner layer 20', once the inner layer 20' of the preform 34 is formed, the outer layer 24' of recycled plastic can be injection or compression molded over the inner layer 20' to provide a multi-layer preform 34. FIG. 3 is a representative example of a preform 34 formed with a thermoformed inner layer 20' and injection molded outer layer 24'. Preforms 34 formed in accordance with the principles of such second preferred embodiment are generally better suited for applications that require a wider opening 13 or dispensing mouth.

The multi-layer container can then be blown using conventional blow molding operations. Because the preform 34 will be stretched and "thinned-out" during the subsequent blow molding process, the thickness of the preform 34 -- at portions corresponding to like portions of the blown container -- will inherently be somewhat thicker. In fact, the thickness of the various portions of the preform 34 are typically designed to take into account the amount of stretch and hoop expansion necessary to form the thickness profile desired in the final container 10. For clarity, hereinafter, the multi-layer containers having inner and outer layers 20, 24 that have not been carbon-treated should be distinguished from containers 10 in which the inner surface 22 has been carbon coated.

After a container having an inner layer 20 and outer layer 24 are produced, a carbon coating is formed on at least a portion of the inner surface 22 of the inner layer 20. The carbon coating 26 does not have to be immediately applied to the container, however, it is generally more efficient to apply the coating 26 promptly after the container has been blown and is within an appropriate temperature profile.

In a preferred embodiment, the blown multi-layer containers are removed from a conventional high-speed rotary blow-molding machine and subsequently transferred, directly or indirectly (i.e., via an intermediate handling step), to an apparatus for applying a carbon coating 26 to the containers. In high-speed production applications, the carbon-coating apparatus will typically also be of the rotary type. An example of such an apparatus that can be used to apply the carbon coating to the inner surface 22 of the container 10 is available from Sidel of Le Havre, France and is commercially marketed under the "ACTIS" trade name.

A method for carbon-coating multi-layer containers 10 is next described in further detail. In accordance with a preferred method for carbon coating the inner surface 22 of the container 10, a conventional carbon-coating or carbon-treating

apparatus having rotary kinematics and a central vertical axis is provided. The carbon-coating apparatus generally rotates about its central vertical axis in a first rotational direction, e.g., counterclockwise, at a fairly high rotational speed. A blow-molding machine, or other rotary container transfer mechanism, located generally in close proximity to the carbon-coating apparatus functions as the source of containers for subsequent carbon-coating treatment. To facilitate the transfer, the rotary container transfer mechanism rotates in a direction opposed to the rotational direction of the carbon-coating apparatus -- e.g., clockwise -- and the multi-layer containers 10 are mechanically shifted from the container transfer mechanism to the carbon-coating apparatus. Although not required for the practice of the present invention, the container 10 preferably includes a neck flange 30 or other physical means for at least partially supporting the container 10 during the mechanical transfer process.

As the containers 10 are transferred from the transfer mechanism to the carbon-coating apparatus, the containers 10 are preferably held by the upper portion 12 in an upright orientation with the opening 13 generally facing upwardly. If desired, a vacuum can also be generated and used to support or partially support the container 10. During the transfer process, the individual containers 10 are received by a receiving mechanism which is part of the carbon-coating apparatus. The receiving mechanism revolves around the central axis of the carbon-coating apparatus, grasps or secures the container, and seals the opening 13 of the upper portion 12 of the container, much like a lid. When properly positioned over and abutting the opening 13, the receiving mechanism produces a tight to "airtight" seal over the container.

The receiving mechanism includes at least two apertures positioned above the opening 13 of the container that are used for the introduction and removal of gases from the inside of the container. A first aperture in the receiving mechanism is in

communication with a vacuum source, such as a vacuum pump. After the receiving mechanism has securely sealed the opening 13, the air within the container is discharged through the first aperture by means of a vacuum. It is desirable that degree of vacuum falls within a range of about 10^{-2} to 10^{-5} torr, so as to shorten the discharge time for a vacuum and saves necessary energy therefor. With a lower degree of vacuum of over 10^{-2} torr, impurities in the container are much increased, on the other hand, with a higher degree of vacuum under 10^{-5} torr, increased time and a large energy are needed to discharge the air in the container.

Once the air inside the container has been evacuated, the container is subsequently filled or "charged" with a raw gas that will be used in the formation of the carbon coating 26. The flow rate of the raw gas is preferably within a range from about 1 to 100 ml/min. Preferably, the diffusion of the raw gas within the container is enhanced by providing an extension, such as a tube having a plurality of blow openings. In accordance with one embodiment, an extension enters inside of the container 10 through the second aperture some time after the opening 13 is sealed and the extension extends to within about 25.4 mm to 50.8 mm (1.0 in. - 2.0 in.) of the lowermost portion of the container.

The raw gas may be comprised of aliphatic hydrocarbons, aromatic hydrocarbons, oxygen containing hydrocarbons, nitrogen containing hydrocarbons, etc., in gaseous or liquid state at a room temperature. Benzene, toluene, o-xylene, m-xylene, p-xylene and cyclohexane each having six or more than six carbons are preferable. The raw gases may be used singularly, but a mixture of two or more than two kinds of raw gases can also be used. Moreover, the raw gases may be used in the state of dilution with inert gas such as argon and helium.

At some point after the container has been received by the receiving mechanism of the carbon-coating apparatus, the container is inserted into a cylinder or other hollow space

provided to accommodate the container. In the preferred embodiment, the carbon-coating apparatus includes a plurality of hollow cylinders that rotate in the same direction as, and in synchronization with, the receiving mechanism. It is further preferred that the receiving mechanism that retains and seals the opening 13 of the container also functions to cover the cylinder.

After the supply of the raw gas into the container, energy is impressed upon the container from a high frequency electric energy source, such as a microwave-producing device. The impression of the electric power generates plasma, and causes extreme molecular excitation ionization and a carbon coating 26 to be formed on the inner surface 22 of the container.

While the foregoing method illustrates one process for forming a carbon coating 26 on the inner surface 22 of a container, other conventional methods can also be used successfully. For instance, the plastic container could instead be inserted and accommodated within an external electrode and have an internal electrode positioned within the container. After the container is evacuated and is charged with raw gas supplied through the internal electrode, electric power is supplied from the high frequency electric source to the external electrode. The supply of electric power generates plasma between the external electrode and the internal electrode. Because the internal electrode is earthed, and the external electrode is insulated by the insulating member, a negative self-bias is generated on the external electrode, so that carbon film is formed uniformly on the inner surface of the container along the external electrode.

When the plasma is generated between the external electrode and the internal electrode, electrons are accumulated on the inner surface of the insulated external electrode to electrify negatively the external electrode, to generate negative self-bias on the external electrode. At the external electrode, a voltage drop occurs because of the accumulated electrons. At

this time, carbon dioxide as the carbon resource exists in the plasma, and positively ionized carbon resource gas is selectively collided with the inner surface 22 of the container which is disposed along the external electrode, and, then, carbons close to each other are bonded together thereby to form hard carbon film comprising remarkably dense coating on the inner surface 22 of the container.

The thickness and uniformity of the carbon coating 26 can be varied by adjusting the output of high frequency; the pressure of the raw gas in the container; the flow rate for charging the container with gas; the period of time during which plasma is generated; the self-bias and kind of raw materials used; and other like variables. However, the thickness of the carbon coating 26 is preferably within a range from 0.05 to 10 μm to obtain the effective suppression of the permeation and/or absorption of the low molecular organic compound and the improved gas barrier property, in addition to an excellent adhesion to plastic, a good durability and a good transparency.

FIG. 4 shows an elevational view of a further embodiment of a container 100 constructed in accordance with the principles of the present invention. Container 100 typically includes an upper wall portion 112, including an opening 113; an intermediate sidewall portion 114 positioning beneath the upper wall portion 112; and a base portion 116 positioned beneath the intermediate sidewall portion 114. The base portion 116 is adapted to support the container 100 either dependently, i.e., where another object such as a base cup (not shown) is used, or independently, i.e., where no other objects are needed to stand the container upright on a generally flat surface. In a preferred embodiment, the container 100 is supported by a freestanding base formed by a plurality of integrally formed feet 118, such as those illustrated in FIG. 4.

Referring to FIGS. 5-7, which represent enlarged detailed views of areas 100A, 100B and 100C, respectively, of FIG. 4, the container 100 includes a molded outer layer 120, having a

vertical length, an inner surface 122, an outer surface 123 and a central vertical axis B. The inner surface 122 of the molded outer layer 120 is at least partially coated with a thin layer or film of carbon 124 as in the embodiments of FIGS. 1-3. While complete encapsulation of the inner layer 120 by the carbon layer 124 is preferred, it may not be required for particular applications. It is preferred that the molded outer layer 120 is substantially coextensive with the carbon layer 124 and provide structural support for the container 100.

The molded outer layer 120 includes at least 50% of recycled plastic material, desirably at least 75% of recycled plastic, and may include as much as 90% recycled plastic material. If desired, the molded outer layer may be 100% recycled plastic material. Preferably, the molded outer layer is formed from recycled polyethylene terephthalate (PET), but the present invention is not limited thereto and virtually any recycled plastic may be conveniently employed.

The molded outer layer 120 is desirably comprised of a thermoplastic material and may utilize the materials listed for the molded inner layer 20 of FIG. 1.

It is particularly desirable to blend small amounts of barrier materials and/or oxygen scavenging or reacting materials with the recycled plastic as discussed with respect to FIG. 1. For example, less than 5% by weight of saran, ethylene vinyl alcohol copolymers (EVOH) and acrylonitrile copolymers, such as Barex. In addition, the present invention can readily use ultra low intrinsic viscosity (IV) material, e.g., material having an IV of less than around 0.60 or 0.55. These materials are frequently white or whitish in color. A significant advantage of the present invention is ability to process in-process scrap simply and efficiently, even with materials as aforesaid.

The inner surface 122 of the outer layer 120 is coated with a thin layer of carbon 124 which provides enhanced barrier properties to the container 100. Features of, characteristics of and preparation of the carbon coating 124 has been described

above with respect to FIG. 1 and this applies also to the embodiments of FIGS. 4-7.

The molded outer layer 120 has a wall thickness, taken along its vertical length, that is in the range of 6 to 23 mils (0.1524 mm to 0.5842 mm). As illustrated in FIGS. 5-7, the thickness of the outer layer can also be separately and independently varied along its vertical length, as with outer layer 24 of FIG. 1. In the same manner as outer layer 24 of FIG. 1, because the molded outer layer 120 is generally comprised of a less expensive plastic material that does not directly contact the contents of the container 100, a less expensive material can be used to form the bulk of the container including a number of the structural integral components for the container, such as the neck flange 126 and outer threads 128 shown in FIG. 4.

Similarly, the inner carbon coating can be readily varied so that the thickness thereof varies along the vertical length of the container. Desirably, however, for convenience a substantially uniform carbon coating is provided.

The embodiments of FIGS. 4-7 offer the significant advantages of the present invention described with respect to FIGS. 1-3.

The container of FIGS. 4-7 may be formed by any of several known processing techniques which permit the manufacture of a single layer or multi-layer blow molded container as described for FIG. 1. In a preferred embodiment, the container 100 is formed via a blow molding operation involving a preform 130, such as the one generally depicted in FIG. 8. Although not a required feature, the preform 130 may include a neck flange 132 (for handling purposes) and outer threads 134 (to secure a closure) that corresponds to the same features shown in FIG. 4. After the blow molding of the container to form the final container 100 an embodiment of which is shown in FIG. 4, but some time before the filling operation, the inner surface 122 of the container is carbon-treated as further discussed above.

In one embodiment shown in FIG. 9, a preform 140 which will become the container is produced by extrusion molding a preform 140 with a preform body 146 and a preform base 148, neck flange 142 and outer threads 144. An extrusion process permits the manufacturer to readily vary the thickness of material being extruded along the length of the extrudate. Variations in the thickness of the preform is desirable for several reasons which include aesthetics, efficient material use and reduced costs, and variable strength requirements.

The preform 140 includes recycled plastic material which, as indicated hereinabove is a particular advantage of the present invention.

In the embodiment of FIG. 8, a preform 130 is produced by thermoforming a thin sheet of plastic material and forming that sheet into what will become the preform 130, or injection or compression molding the preform 130. Thus, preform 130 of FIG. 8 may include a neck flange 132 and outer threads 134, body portion 136 which will become the container body portion and base portion 138 which will become the container base portion. The container can then be blown using conventional blow molding operations as described above.

After the preform has been formed into an intermediate container by blow molding, a carbon coating is formed on at least a portion of the inner surface 122 of the container 120 and preferably on the entire inner surface, as described above for FIG. 1. The carbon coating 124 does not have to be immediately applied to the container, however, it is generally more efficient to apply the carbon coating promptly after the intermediate container has been blown and is within an appropriate temperature profile.

The container of FIG. 4 offers significant advantages in addition to those of FIG. 1. The base container is a mono-layer material that can be readily processed by conventional means. Moreover, the recycled base material can be readily admixed with other materials and due to the inner carbon coating does not

contact the container contents. Moreover, barrier properties are readily and easily obtained and the container contents are not impacted by adverse aromas or taste. Further, the container of the present invention eliminates the need for a separate barrier liner or a virgin liner. The small amount of inner carbon coating dos not adversely affect recycling, and colored materials can be readily used to provide a desirably colored container, for example, the outer layer can be easily colored in a desirable commercial color.

The container of FIG. 4 offers the significant advantages of a mono-layer container with desirable engineered properties, as barrier resistance and low cost. Thus, processing is significantly easier than with multi-layer containers since one is working with a mono-layer material without the necessity for the use of liners and complicated coinjection processing. Further, one can blend the recycled plastic with other materials to readily obtain special properties while still retaining the use of desirably low cost recycled plastic. For example, one could customize the product in order to obtain desirable characteristics while still using recycled material and a mono-layer material.

The internal carbon coating is simply and conveniently applied and is quite thin and yet precludes the migration of adverse flavors and taste into the contents of the container. It is particularly desirable to use a variety of colors for the recycled plastic as for example an amber color for beer. It would be highly desirable to use such a container as in the present invention with a tailored color and for a beer or soft drink or juice product. As a still further alternative, one could blend heat resistant plastic with the recycled plastic to obtain highly desirable characteristics.

Although certain preferred embodiments of the present invention have been described, the invention is not limited to the illustrations described and shown herein, which are deemed to be merely illustrative of the best modes of carrying out the

invention. A person or ordinary skill in the art will realize that certain alternatives, modifications, and variations will come within the teachings of this invention and that such alternatives, modifications, and variations are within the spirit and the broad scope of the appended claims.

90年6月3日修正/更正/補充

AMENDED CLAIMS

1. A blow molded mutli-layer container including an upper wall portion having an opening; an intermediate sidewall portion positioned beneath the upper wall portion; and a base portion positioned beneath the intermediate sidewall portion and adapted to support the container, the container comprising:

a molded inner layer formed from a plastic material having a vertical length and an inner surface;

a molded outer layer including recycled plastic that is substantially coextensive with the inner layer; and

a carbon coating formed on the inner surface of the inner layer,

wherein the outer layer comprises at least 0.40 by weight of the overall weight of the container.

2. A blow molded multi-layer container according to claim 1, wherein the inner layer is formed from a plastic material comprised of a resin selected from the group consisting of polyethylene resin, polypropylene resin, polystyrene resin, cycloolefine copolymer resin, polyethylene terephthalate resin, polyethylene naphthalate resin, ethylene-(vinyl alcohol) copolymer resin, poly-4-methylpentene-1 resin, poly(methyl methacrylate) resin, acrylonitrile resin, polyvinyl chloride resin, polyvinylidene chloride resin, styrene-acrylo nitrile resin, acrylonitrile-butadiene-styrene resin, polyamide resin, polyamideimide resin, polyacetalresin, polycarbonate resin, polybutylene terephthalate resin, ionomer resin, polysulfone resin, polytetra fluoroethylene resin, and combinations of two or more of such resins.

3. A blow molded multi-layer container according to claim 1, wherein the inner layer is formed from a process selected from the group consisting of extrusion and thermoforming, and wherein the outer layer is formed from a process selected from

the group consisting of injection molding and compression molding.

4. A blow molded multi-layer container according to claim 1, wherein the inner layer includes a material selected from the group consisting of a virgin plastic material, a barrier material, an oxygen-scavenging material, and material that is a combination of a barrier and oxygen-scavenger.

5. A blow molded multi-layer container according to claim 1, wherein at least one of the inner layer and the outer layer has a thickness that varies along its vertical length.

6. A blow molded multi-layer container according to claim 1, wherein the thickness of the inner layer and outer layer are controllably varied with respect to one another.

7. A blow molded multi-layer container according to claim 1, wherein the thickness of the inner layer along the intermediate portion of the container is less than 0.15 the thickness of the outer layer.

8. A blow molded multi-layer container according to claim 1, wherein the thickness of the carbon coating is less than 10 μm and the weight of the carbon coating is less than about 1/10,000th of the total weight of the container.

9. A blow molded multi-layer container according to claim 1, wherein the carbon coating is amorphous.

10. A blow molded multi-layer container according to claim 1, wherein the carbon coating has one of a generally uniform thickness, and a thickness that varies along its vertical length.

11. A blow molded multi-layer container according to claim 1, including at least one of the upper portion of the container including a support flange, and the base portion including a plurality of feet.

12. A container according to claim 1, wherein said container is filled with contents.

13. A container according to claim 12, wherein said container is filled with food products.

14. A container according to claim 12, wherein said container is filled with contents selected from the group consisting of beer, soft drinks and juice.

15. A container according to claim 12, wherein said carbon coating protects the contents of the container.

16. A container according to claim 12, wherein said container precludes the migration of adverse flavors and tastes into the container contents.

17. A container according to claim 12, wherein said container affords protection from oxygen and carbon dioxide permeation.

18. A blow molded multi-layer container including an upper wall portion having an opening, an intermediate sidewall portion positioned beneath the upper wall portion, and a base portion positioned beneath the intermediate sidewall portion and adapted to support the container, said container further comprising: a molded outer layer having an inner surface and an outer surface and formed from at least 40% of recycled plastic; a carbon coating formed adjacent the inner surface of the outer layer and adhered thereto and substantially coextensive with the outer layer, wherein said carbon coating has a thickness less than about 10 microns, wherein said container can be recycled.

19. A container according to claim 18, wherein said outer layer has a thickness from 6 to 23 mils, and wherein the carbon coating has a thickness of 0.05 to 10 microns.

20. A container according to claim 18, wherein the thickness of the outer layer varies so that the intermediate sidewall portion is thinner than the upper wall portion and the base portion.

21. A container according to claim 18, including a barrier material added to the outer layer.

22. A container according to claim 18, wherein the carbon is coated on the inner surface of the blow molded container from at least one gaseous hydrocarbon.

23. A container according to claim 18, wherein the carbon coating is amorphous.

24. A container according to claim 18, wherein the carbon coating has one of a generally uniform thickness, and a thickness that varies along the vertical length of the container.

25. A container according to claim 18, including at least one of the upper portion of the container including a support flange, and the base portion includes a plurality of feet.

26. A container according to claim 18, wherein the outer layer is colored.

27. A container according to claim 18, wherein the outer layer includes at least 75% of recycled plastic.

28. A method of manufacturing a container coated with a carbon coating, which comprises:

providing a container including an upper wall portion having an opening, an intermediate side wall portion positioned beneath the upper wall portion, and a base portion positioned beneath the intermediate wall portion;

enclosing the container within a hollow space provided to accommodate the container;

discharging the air within the container creating a vacuum;

charging the internal volume of the container with raw gas; and

inducing the formation of a carbon coating on the inner surface of the container.

29. A method according to claim 28, wherein said container is a multi-layer container including a plastic inner layer having a vertical length and an outer layer including recycled plastic substantially coextensive with the inner layer, wherein

the outer layer comprises at least 0.40 of the overall weight of the container.

30. A method according to claim 29, wherein the multi-layered container is formed by extruding a plastic sleeve from a thermoplastic material; injection molding an outer layer over the sleeve to form a preform; and blow molding the preform to form a multi-layer container.

31. A method according to claim 29, wherein the thickness of the inner layer varies along its vertical length.

32. A method according to claim 29, wherein the inner layer includes a material selected from the group consisting of a barrier material, an oxygen-scavenging material, and a material that is a combination of a barrier and an oxygen-scavenger.

33. A method according to claim 28, wherein the raw gas is selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, oxygen containing hydrocarbons, and mixtures of two or more of such gases.

34. A method according to claim 28, wherein the formation of the carbon coating on the inner surface of the container is induced by a high frequency electric source.

35. A method according to claim 34, wherein the high frequency electric source includes an internal electrode and an insulated external electrode for generating negative self-bias.

36. A method according to claim 28, wherein the formation of carbon coating on the inner surface of the container is induced by a microwave.

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ABSTRACT OF THE DISCLOSURE

A blow molded container having barrier properties and including an upper wall portion having an opening, an intermediate sidewall portion positioned beneath the upper wall portion, and a base portion positioned beneath the intermediate sidewall portion to support the container. The container includes a molded outer layer having an inner surface and an outer surface formed from at least 40% of recycled plastic, and a carbon coating formed on the inner surface of the outer layer and adhered thereto and substantially coextensive with the outer layer, wherein said carbon coating has a thickness of less than about 10 microns. A blow molded multi-layer container is also provided having an upper wall portion, including an opening; an intermediate sidewall portion positioned beneath the upper wall portion; and a base portion positioned beneath the intermediate sidewall portion, the base portion being adapted to dependently or independently support the container. The container includes (i) a molded inner layer formed from a plastic material, the inner layer having a vertical length and a carbon-treated inner surface; and (ii) a molded outer layer formed from recycled plastic that is substantially coextensive with the inner layer.

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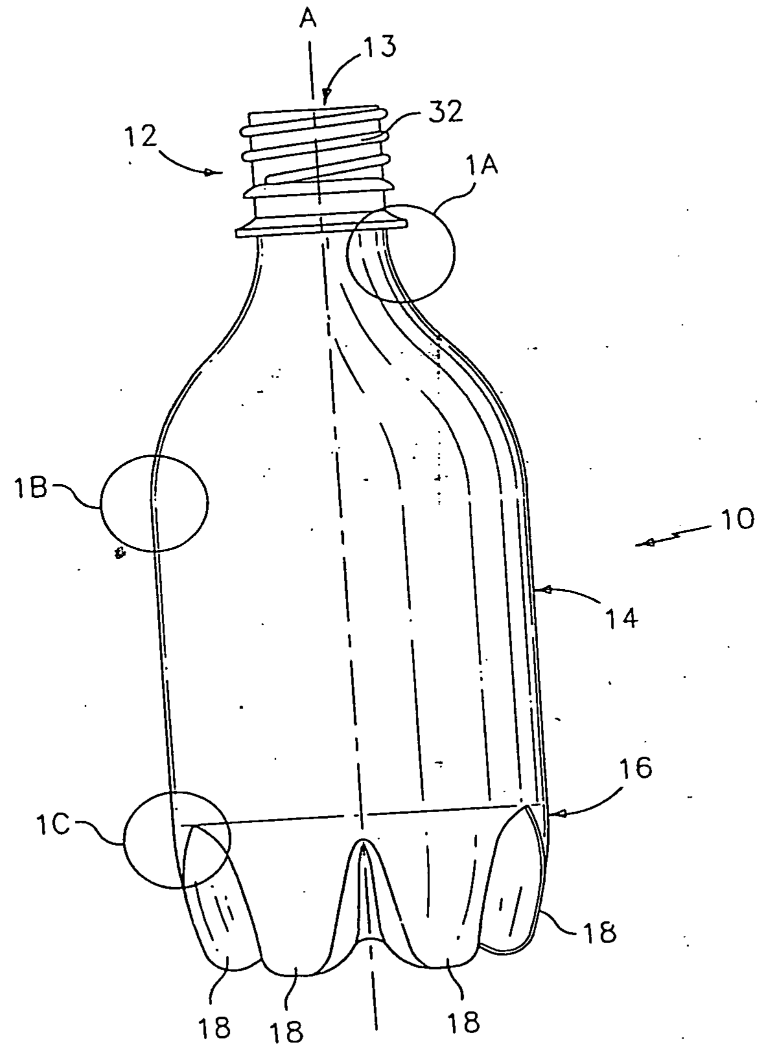

FIG. 1

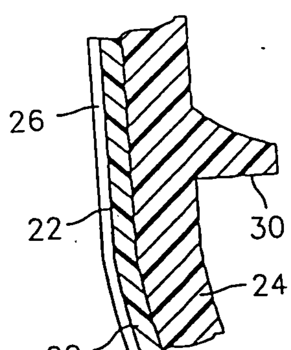

FIG. 1A

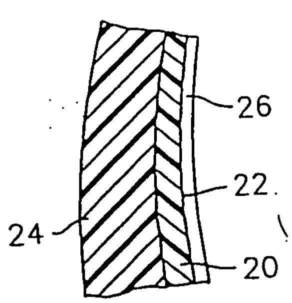

FIG. 1B

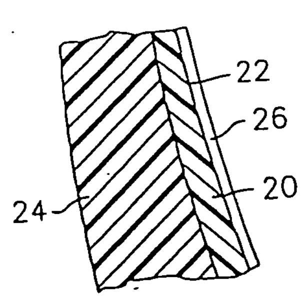

FIG. 1C

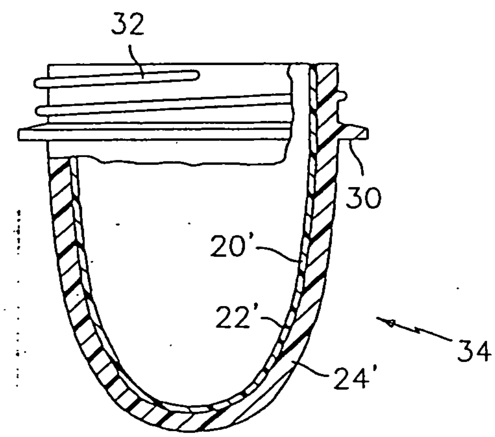

FIG. 3

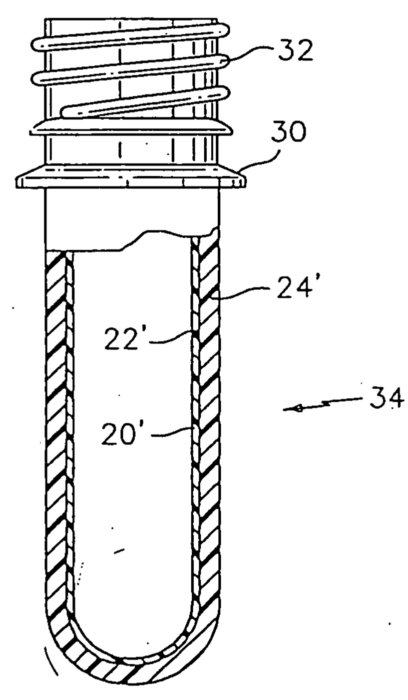

FIG. 2

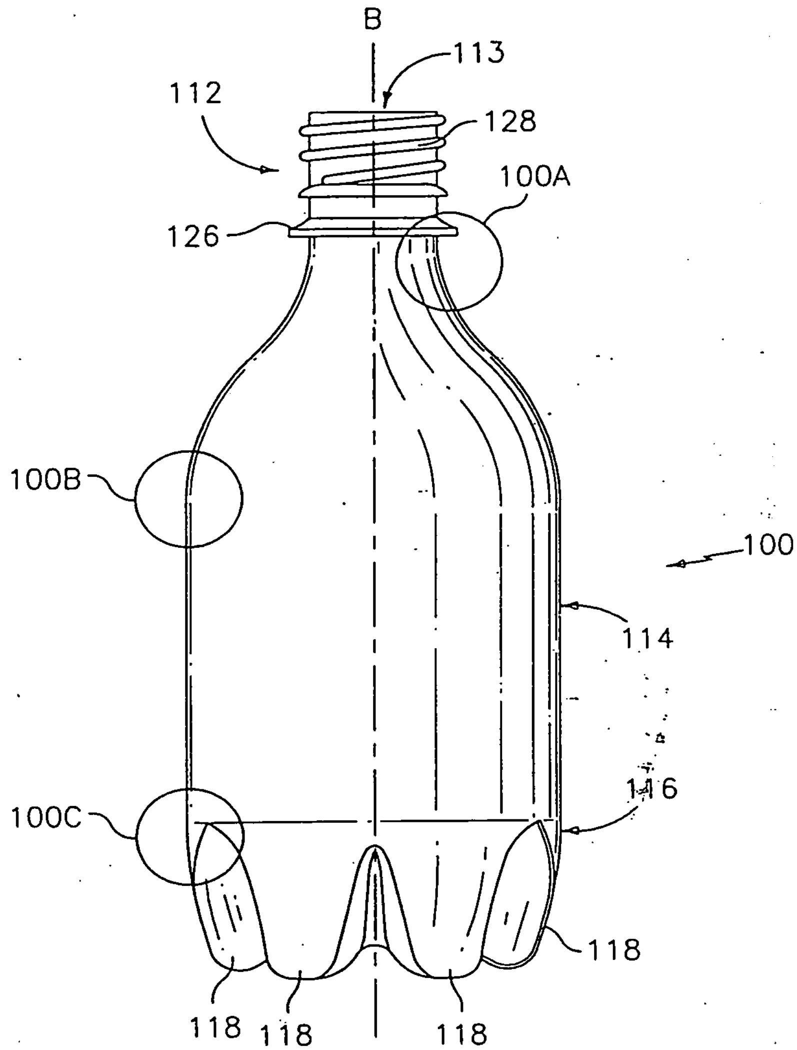

FIG. 4

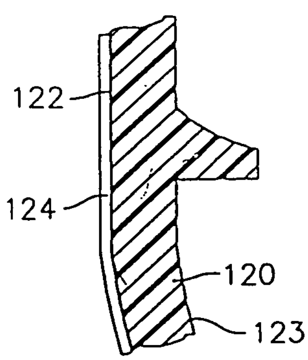

FIG. 5

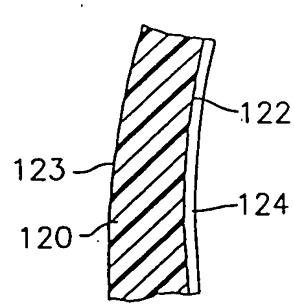

FIG. 6

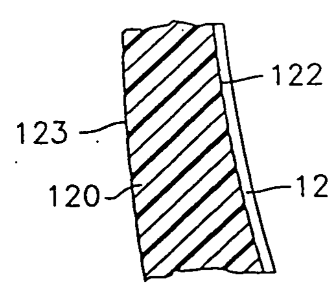

FIG. 7

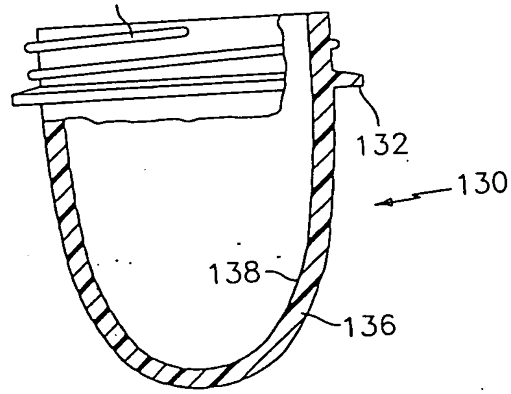

FIG. 8

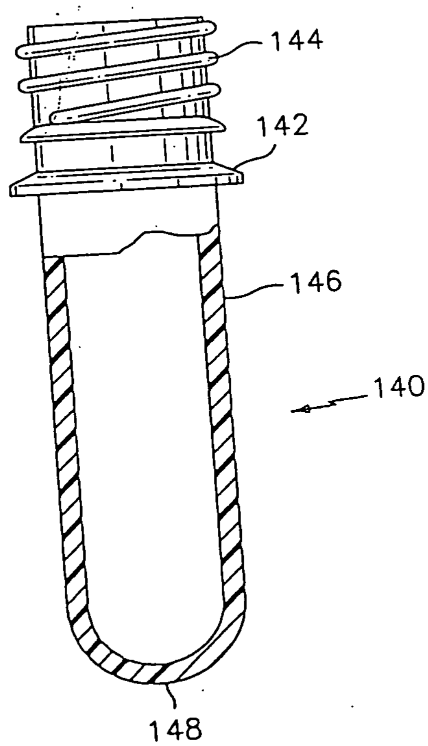

FIG. 9

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初審（前審）引證附件
再審

引証案1
(31481)

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B65D1/02

[54]名　　稱：具有以碳處理之內表面的塑膠容器

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[31]09/525,871 [32]2000/03/14 [33]美國

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[57]申請專利範圍：

1.一種吹塑多層容器，其包括一具有開口之上壁部份；一位置在上壁部份下方之中間側壁部份；以及一位置在中間側壁部份下方且用於支撐該容器之底部，該容器含有：
從塑膠材料所形成之一模塑內層，其具有垂直長度與內部表面；
包含回收塑膠之一模塑外層，其本質上係與內層共同擴張；以及
一在內層之內部表面上形成之碳塗覆物，
其中該外層至少含有佔容器總量之0.40之重量。

2.根據申請專利範圍第1項之吹塑多層容器，其中內層係選自由聚乙烯樹脂、聚丙烯樹脂、聚苯乙烯樹脂、環烯烴共聚物樹脂、聚對苯二甲酸乙二酯樹脂、聚萘二甲酸乙二酯樹脂，乙烯-(乙烯醇)共聚物樹脂、聚-4-甲基戊烯-1樹脂、聚(甲基丙烯酸甲酯)樹脂、丙烯腈樹脂、聚氯乙烯樹脂、聚偏氯乙烯樹脂、苯乙烯-丙烯腈樹脂、丙烯腈-丁二烯-苯乙烯樹脂、聚醯胺樹脂、聚醯胺醯亞胺樹脂、聚甲醛樹脂、聚碳酸酯樹脂、聚對苯二甲酸丁二酯樹脂、離聚物樹脂、聚碸樹脂、聚四氟乙烯樹脂、與此樹脂之二或多種之合併所組成之族群中之樹脂所組成之塑膠材料所生成。

3.根據申請專利範圍第1項之吹塑多層容器，其中內層係選自由擠出與熱成型所組成之族群中之方法所形成，且其中外層係選自由射出成型與壓縮模望所組成之族群中之方法所形成。

4.根據申請專利範圍第1項之吹塑多層容器，其中該內層包括一選自由未使用過之塑膠材料、阻隔材料、氧氣清除材料、與阻隔與氧氣清除之組合之材料所組成之族群中之材料。

5.根據申請專利範圍第1項之吹塑多層容

器，其中內層與外層之至少一個係具有沿著其垂直長度改變之厚度。

6.根據申請專利範圍第1項之吹塑多層容器，其中內層與外層之厚度係隨著彼此可控制地改變。

7.根據申請專利範圍第1項之吹塑多層容器，其中內層沿著容器中間部分之厚度係低於外層厚度之 0.15 。

8.根據申請專利範圍第1項之吹塑多層容器，其中碳塗覆物之厚度係低於10微米，且碳塗覆物之重量係約低於容器總重之萬分之一。

9.根據申請專利範圍第1項之吹塑多層容器，其中碳塗覆物係無定形的。

10.根據申請專利範圍第1項之吹塑多層容器，其中碳塗覆物具有通常是均勻之厚度與沿著其垂直長度改變之厚度之其中之一。

11.根據申請專利範圍第1項之吹塑多層容器，其至少包括一包括支撐邊緣之容器之上方部分與一包括數個腳部之底部之其中之一。

12.根據申請專利範圍第1項之容器，其中該容器係填充內容物。

13.根據申請專利範圍第12項之容器，其中該容器係填充食用產品。

14.根據申請專利範圍第12項之容器，其中該容器係填充選擇自由啤酒、軟性飲料及果汁所組成之族群的內容物。

15.根據申請專利範圍第12項之容器，其中該碳塗覆物保護容器之內容物。

16.根據申請專利範圍第12項之容器，其中該容器阻隔不利的風味及味道移入容器內容物中。

17.根據申請專利範圍第12項之容器，其中該容器提供氧氣及二氧化碳滲透的保護。

18.一種吹塑多層容器，其包括一具有開口之上壁部份、一位置在上壁部份下方之中間側壁部份，以及位置在中間

側壁部份下方且用於支撐容器之底部，該容器進一步含有：具有內部表面與外部表面且至少從40%之回收塑膠所形成之模塑外層；與在外層之內部表面相鄰處形成且附著至其上且本質上與外層共同擴張之碳塗覆物，其中該碳塗覆物具有低於約10微米之厚度，其中該容器係可以回收。

19.根據申請專利範圍第18項之容器，其中該外層具有從6至23密爾之厚度，且其中碳塗覆物具有0.05至10微米之厚度。

20.根據申請專利範圍第18項之容器，其中外層之厚度係加以改變以便中間側壁部份比上壁部份與底部更薄。

21.根據申請專利範圍第18項之容器，包括加入阻隔材料至外層中。

22.根據申請專利範圍第18項之容器，其中碳係從至少一個氣體烴類塗覆至吹塑容器之內部表面上。

23.根據申請專利範圍第18項之容器，其中碳塗覆物係無定形的。

24.根據申請專利範圍第18項之容器，其中碳塗覆物具有通常是均勻之厚度與沿著其垂直長度改變之厚度之其中之一。

25.根據申請專利範圍第18項之容器，其至少包括一包括支撐邊緣之容器之上方部分與一包括數個腳部之底部之其中之一。

26.根據申請專利範圍第18項之容器，其中外層係有顏色的。

27.根據申請專利範圍第18項之容器，其中外層包括至少75%之回收塑膠。

28.一種製造以碳塗覆物塗覆之容器之方法，其含有：

提供一容器，其包括一具有開口之上壁部份，一位置在上壁部份下方之中間側壁部份；以及一位置在中間側壁部份下方之底部：

在提供以容納容器之中空空間中封入容器；

排出容器中之空氣以產生真空；

飼入生氣體至容器之內部體積中；以及

使碳塗覆物在容器之內部表面上形成。

29.根據申請專利範圍第28項之方法，其中該容器係多層容器，其包括具有垂直長度之塑膠內層以及包括回收塑膠且本質上與內層共同擴張之外層，其中外層至少含有容器總重之 0.40。

30.根據申請專利範圍第29項之方法，其中多層容器之形成係藉從熱塑性材料擠壓塑膠套筒；在套筒上射出成型一外層以形成預成型物；以及吹塑預成型物以形成一多層容器。

31.根據申請專利範圍第29項之方法，其中內層之厚度係沿著其垂直長度而改變。

32.根據申請專利範圍第29項之方法，其中該內層係包括一選自由阻隔材料、氧氣清除材料、與阻隔與氧氣清除之組合之材料所組成之族群中之材料。

33.根據申請專利範圍第28項之方法，其中生氣體係選自由脂族烴類、芳香族烴類、含氧烴類、與此氣體之二或多個之混合物所組成之族群中。

34.根據申請專利範圍第28項之方法，其中在容器之內部表面上之碳塗覆物之形成係藉高頻電源以誘導。

35.根據申請專利範圍第34項之方法，其中高頻電源包括內部之電極以及一用於產生負自給偏壓之絕緣外部電極。

36.根據申請專利範圍第28項之方法，其中在容器之內部表面上之碳塗覆物之形成係藉微波以誘導。

圖式簡單說明：

第一圖係一根據本發明之原則之容器之正視圖。

第一圖A、第一圖B與第一圖C係容器各個區域之截面與放大圖，其中係說明形成容器之層之相對厚度。

第二圖係多層預成型物之一實例之部份切開之正視圖。

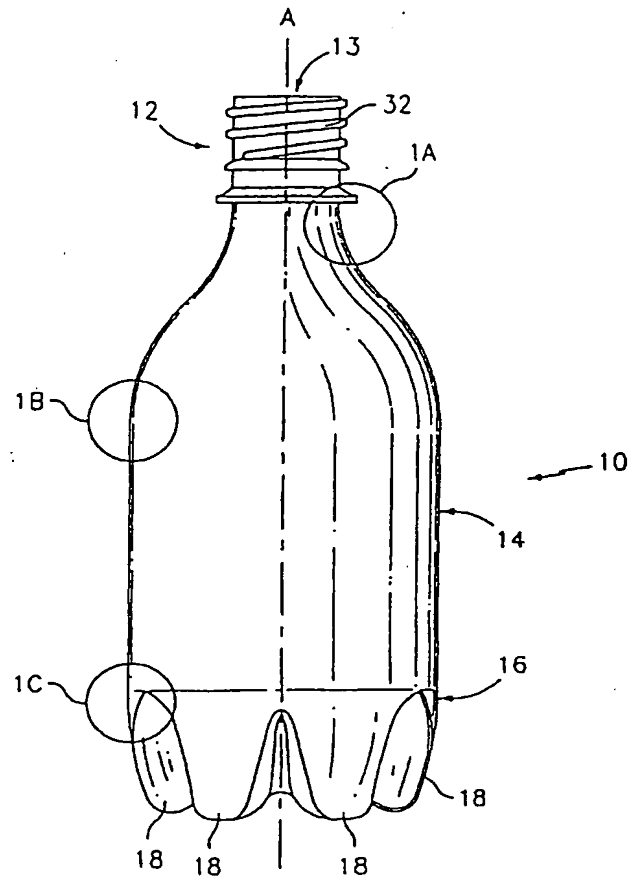
第三圖係多層預成型物之另一實例之部份切開之正視圖。

第四圖係一根據本發明之原則之容器之正視圖。

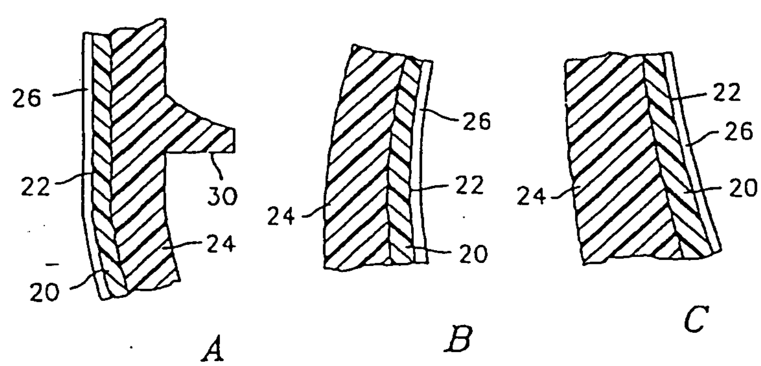
第五圖、第六圖與第七圖係容器各個區域之截面與放大圖，其中係說明形成容器之層之相對厚度。

第八圖係預成型物之一實例之部份切開之正視圖。

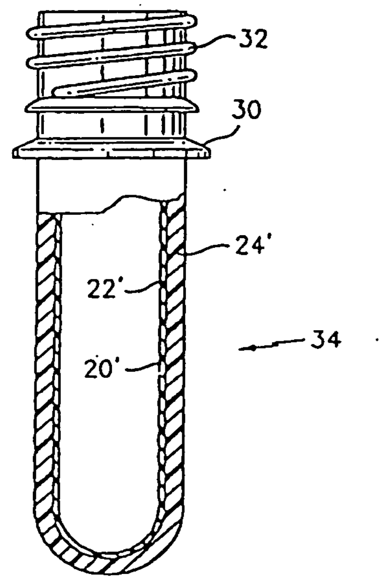
第九圖係預成型物之另一實例之部份切開之正視圖。


A
13
12
32
1A
1B
10
14
16
1C
18
18
18
18

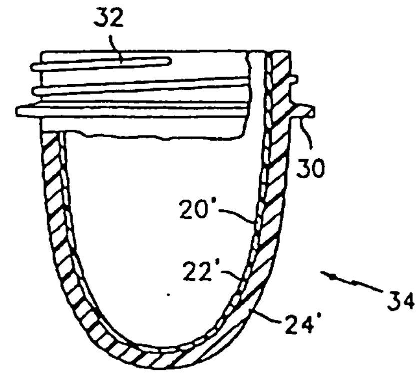
第一圖


26
22
30
24
20
A
26
22
24
20
B
22
26
24
20
C

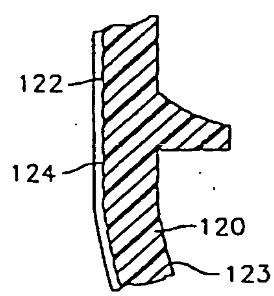
第一圖



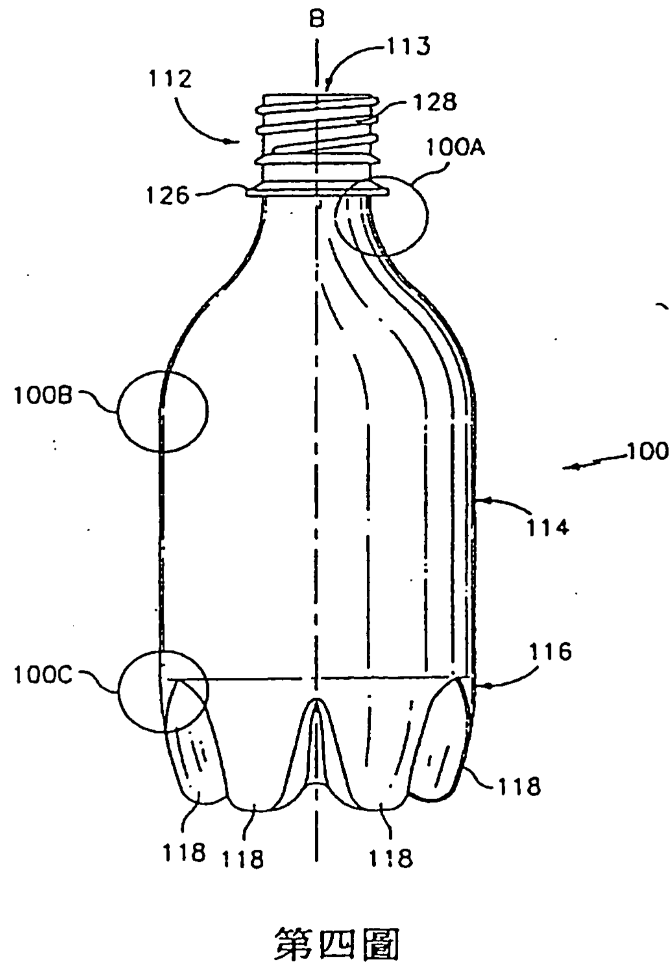
第二圖



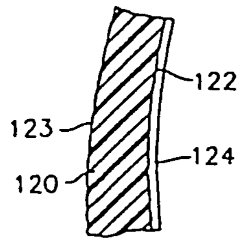
第三圖



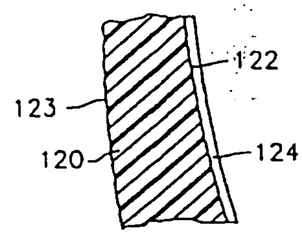
第五圖



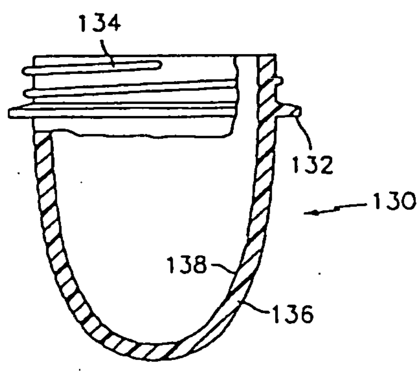
第四圖



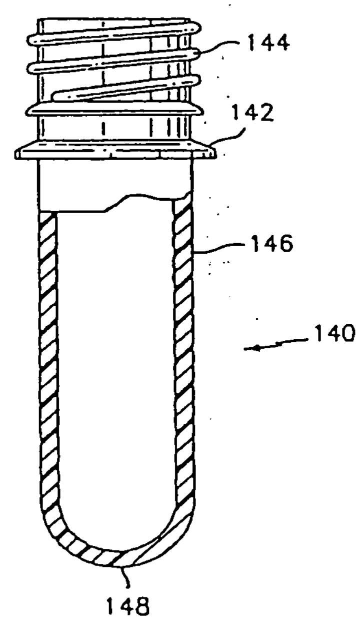
第六圖



第七圖



第八圖



第九圖